Iminophosphine Complexes of Palladium and Platinum: Catalysis and Metallacycloalkanes Synthesis

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CHAPTER 1

IMINOPHOSPHINE LIGANDS AND THEIR COMPLEXES IN SYNTHESIS AND CATALYSIS

This review covers the iminophosphine ligands as a subset of bidentate, heterodonor ligands, and highlights their diverse structural motifs. Because they are commonly used as supporting ligands in coordination chemistry and catalysis, there is a broad range of synthetic and catalytic reactions in which the ligands and their complexes are applied.

1.1 INTRODUCTION

Ligand design is becoming an increasingly important part of synthetic organometallic and coordination chemistry.[1] This is because the properties of metal complexes in synthesis and catalysis are a direct result of the interactions between the metal centre and its supporting ligands.[2] Ligands composed of significantly different chemical functionalities such as hard and soft donor moieties, often called hybrid ligands, find increasing use in molecular chemistry. A special class of these ligands is that of hemilabile ligands. The concept of hemilability was introduced in 1979 by Rauchfuss[3,4] to describe multidentate ligands that 'would bind well enough to the metal centre to allow isolation of the complex, but would readily dissociate the hard end component thus generating a vacant site for substrate binding'[5] (Figure 1.1).[6]

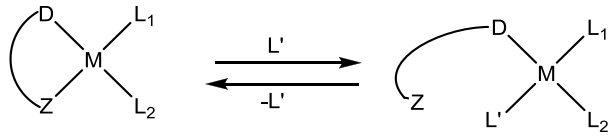


Figure 1.1: Generalized description of adaptive coordination of hemilabile ligands (M = metal centre, D = strong donor, Z = weak donor and L' = substrate).

This is a particularly desirable characteristic for complexes which might have application in catalysis, and since the majority of metals used in such systems are middle or late transition metals, it is usually the soft donor atom which is continually bound to the metal centre.[7] An important property of these ligands is that they can stabilize metal ions in a variety of oxidation states and geometries, which form during the catalytic cycle.[4] In addition, the hard ends are weakly coordinated to the soft metal centre, and can be easily dissociated in solution, affording a vacant site whenever demanded, whereas the chelate effect confers stability to the catalyst precursor in the absence of substrate[4] thereby preventing catalyst decomposition/deactivation.

Over the past few decades, interest in metal complexes of this type of ligands, which are essentially functionalized phosphine ligands, and their role in catalysis has been steadily growing as the different features associated with each donor atom confer unique properties to their metal complexes.[7b,8-10] Unlike homo-donor chelate ligands, hetero-donor ligands have a distinct *trans* effect which can play a role in controlling the selectivity/activity, especially in co- and/or polymerization processes.[11] The syntheses and reactivity/catalytic activity of complexes bearing hemilabile ligands of the type P^N[4,12] and P^O,[13] have been widely reported.

Of the reported hemilabile ligands, those bearing phosphorus and nitrogen atoms as their donors form the most commonly used class. These ligands can display quite different coordination modes compared to the homo-donor P^P and N^N ligands. The π-acceptor character of the phosphorus ligand can stabilize a metal centre in a low oxidation state, while the σ-donor ability of the nitrogen donor makes the metal centre more susceptible to oxidative addition reactions. This combination can help to stabilize intermediate oxidation states and geometries which form during the catalytic cycle.[4,11]

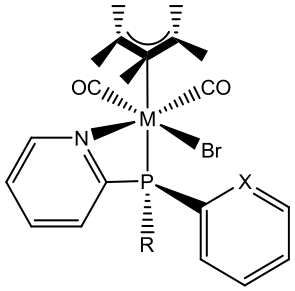
This electronic asymmetry can also be used to optimize a ligand for a particular reaction by appropriate choice of the nature of the donor atoms. For example, binding the phosphorus atom directly to a more electronegative atom such as oxygen or nitrogen[12,14] will reduce its electron donating capability while also enhancing its π-acceptor capacity. On the other hand, the presence of an imino rather than amino group will result in a nitrogen donor atom of greater σ-donating capabilities.[12,15] Moreover, this type of ligands allows modulation of the steric crowding around the metal centre through the simple variation of the substituents on the imine and phosphine groups.[16]

Finally, the past decade or so has witnessed an unprecedented increase in the number of reports on chiral iminophosphine ligands. Complexes based on these ligands have been successfully used in asymmetric catalytic reactions such as hydosilylation,[17] hydroboration of olefins,[18] transfer hydrogenation of ketones[19] to name but a few. Their success is based not only on steric factors, but also on electronic asymmetry on the metal centre generated by the presence of very different donor atoms on the metal,[4,5] a concept that was called electronic differentiation by Faller.[7a,7c]

1.2 CYCLIC IMINE N-DONOR LIGANDS

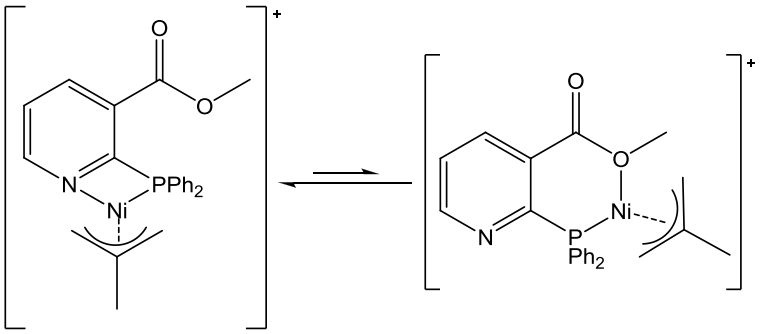
1.2.1 Pyridine-Based Ligands

Pyridylphosphines represent one of the most widely used classes of iminophosphine ligands. The simplest of these is 2-(diphenylphosphino)pyridine. Although this ligand is better suited to bridge two metal centres, there are examples of complexes where it acts as a bidentate hemilabile ligand (complex **1.1**), forming a 4-membered chelate ring with the metal centre.[20]



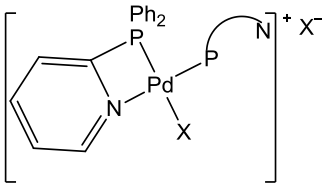
1.1: M = Ru, Mo; X = N

Cationic complexes **1.2** and **1.3** were prepared from the reaction of methyl 2-(diphenylphosphino)nicotinate with a nickel precursor. X-ray crystallographic data revealed that, although this ligand is potentially a tridentate P,N,O ligand, the preferred structures are the bidentate P^N or P^O complexes **1.2** and **1.3** respectively.[21a,21b]



1.2 **1.3**

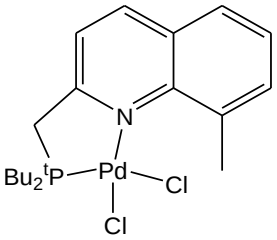
Drent and co-workers[21c,21d] developed a highly efficient class of homogeneous palladium cationic catalysts, **1.4**, for the carbonylation of alkynes. These catalysts allowed the development of cost-effective, large scale production of methyl methacrylate (MMA), a large-scale chemical intermediate for the production of homopolymers and copolymers.



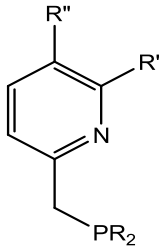
1.4

Due to the unprecedented high selectivities shown by these catalysts, this process has the benefit of exerting minimal negative environmental impact.

5-membered chelate rings can be formed with a metal centre when ligands derived from 8-phosphinoquinoline or phosphines linked to the pyridyl moiety by a methylene linker are used. These complexes are more stable than those that have 4-membered chelate ring structures due to reduced ring strain. Examples of such complexes include the palladium complex **1.5** reported by Deeming and co-workers[22] as well as rhodium complexes of ligands **1.6** – **1.9** reported by Lavigne, Lugan and co-workers.[23]



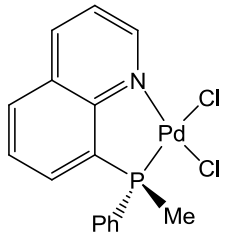
1.5



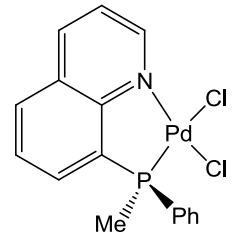
1.6: R = Ph; R' = Me; R" = H
1.7: R = Ph; R' = C_4H_4; R" = C_4H_4
1.8: R = Cy; R' = Me; R" = H
1.9: R = Cy; R' = C_4H_4; R" = C_4H_4

Rhodium complexes of ligands **1.6** – **1.9** were tested for activity in transfer hydrogenation using a wide range of ketones as substrates. The complexes showed good activities, with high turnover frequencies and high enantioselectivities.

The chiral ligand 1-(2-diphenylphosphino-3,6-dimethoxyphenyl)-isoquinoline reacts with palladium precursors to give a racemic mixture of the complex [Pd(P^N)Cl_2], **1.10** and **1.11**.[24]



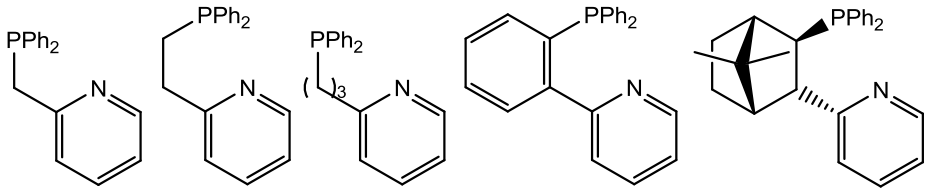
1.10



1.11

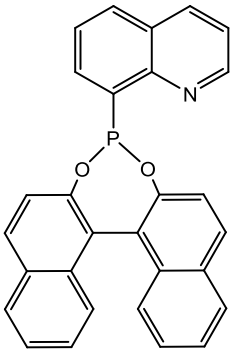
Kamer and co-workers reported the synthesis of ligands **1.12** – **1.16** and their corresponding neutral nickel and palladium complexes as well as cationic palladium complexes.[25] These complexes were tested for activity in ethylene oligomerization. Upon activation with MAO, the nickel complexes were found to be highly active while both the neutral and cationic palladium complexes showed very low activities. Butenes were the major products in all cases. The

ligands all consist of a diphenylphosphine moiety and a 2-pyridyl group and differ in the backbone connecting these functionalities. Ligands **1.12** – **1.14** have respectively one, two and three methylene units as the backbone. Ligand **1.15** has a two-carbon bridge integrated in a phenylene ring between the 2-pyridyl and the phosphine moiety. As in **1.12** – **1.14**, the two-carbon bridge in **1.16** is aliphatic. However, due to this spacer being part of a substituted ring system, the backbone in these ligands is more rigid than in ligands **1.12** – **1.14**.[25]

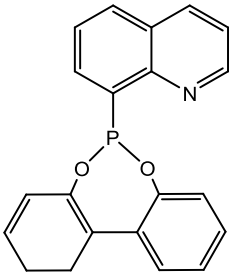


1.12 **1.13** **1.14** **1.15** **1.16**

Electronic asymmetry can be used to optimize ligands for use in a particular reaction by appropriate choice of the nature of the donor atoms. For example, bonding a phosphorus atom directly to a more electronegative atom such as oxygen or nitrogen will reduce its electron-donating capability while enhancing its π-acceptor capacity.[11] This reduction in σ-donor ability leads to increased electrophilicity in their resultant metal complexes, facilitating easy binding of olefinic substrates such as ethylene and styrene. The overall result is increased catalytic activity of these complexes. Consiglio and co-workers reported the synthesis and complexation, to palladium and nickel, of ligands **1.17** – **1.20**.[26] The palladium complexes were tested for activity in the copolymerization of styrene and ethylene with carbon monoxide while the nickel complexes were tested for activity in ethylene oligomerization. The nickel complexes were found to be highly active at ambient temperature and low ethylene pressure (1 – 2 bar) and the major products were found to be C_4 and C_6 oligomers.[26]



1.17



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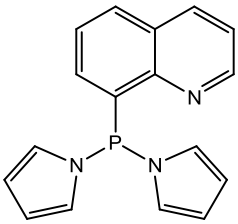

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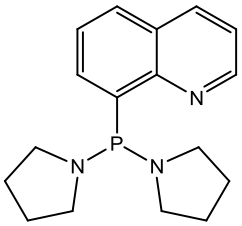
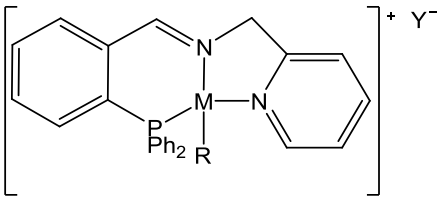


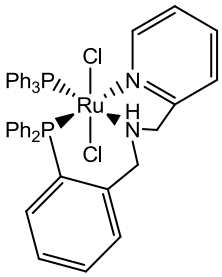
1.20

Vrieze and co-workers prepared palladium and platinum complexes of the type **1.21**, based on a multifunctional and hemilabile phosphorus-bis(nitrogen) ligand, which combined both imine and pyridyl moieties.[27] The ligand was found to coordinate in a terdentate fashion to group 10 metals, resulting in the formation of cationic complexes of the type $[M^{II}(PNN)(R)]Y$, where M = Pd, Pt; R = alkyl, acetyl or η^1-allyl and Y = Cl, CF_3SO_3. Catalytic studies showed that the palladium conplexes were highly active in allylic alkylation reactions.

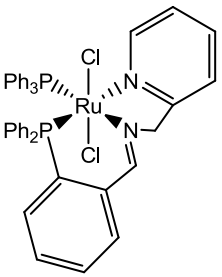


1.21

Del Zotto, Baratta and co-workers prepared similar ligands and tested their rhodium complexes **1.22** – **1.26** for activity in the transfer hydrogenation of ketones.[15a] They reported that complex **1.26** catalyzes the quantitative reduction of acetophenone to 1-phenylethanol with high turnover frequencies. Replacing the amino complex with amino derivatives **1.23** and **1.24** resulted in slightly lower turnover frequencies, but these complexes still showed comparable activities to those reported by other groups.[14a,28]



1.22



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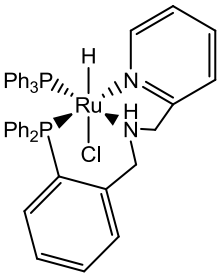
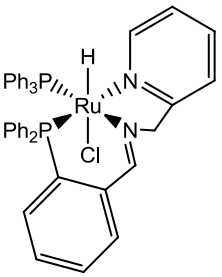
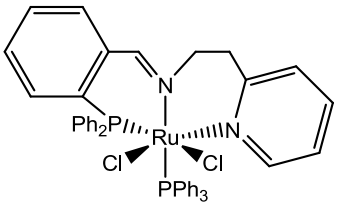


1.24

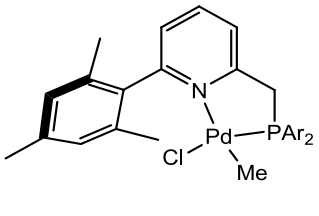


1.25

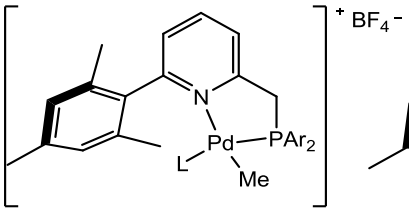


1.26

Liu and co-workers prepared bulky pyridylphosphine ligands (6-mesityl-2-((diaryl)methyl)pyridine by the Suzuki coupling of mesitylboronic acid with 6-bromo-2-picoline followed by phosphinylation.[29] Palladium (**1.27**, **1.28**) and nickel (**1.29**) complexes were prepared by reaction of these ligands with [Pd(COD)(Me)Cl] and [Ni(DME)Br]. The cationic methylpalladium(II) complexes, **1.28**, performed poorly in catalytic ethylene polymerization and could only catalyze ethylene dimerization and trimerization.[30] The nickel complexes, on the other hand, were found to be efficient catalysts upon activation by methylaluminoxane (MAO). The nickel complexes catalyzed the polymerization of ethylene when an Al/Ni ratio of 150 was used whereas dimerization and trimerization was observed when the Al/Ni ratio was increased to 500.[29]

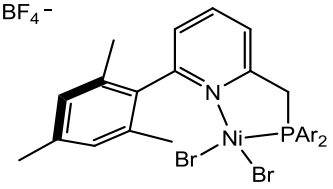


1.27a, 1.27b



1.28a, 1.28b

a: Ar = Mes, L = NCMe
b: Ar = 2-Tol, L = NCMe

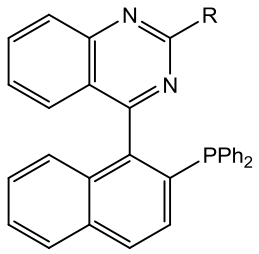


1.29a, 1.29b

1.2.2 Quinazoline-Based Ligands

Guiry and co-workers prepared a series of quinazoline-based ligands, **1.30** – **1.35** and found them to be effecient ligands in palladium-catalyzed allylic alkylation reactions.[31] Ligand **1.31**,

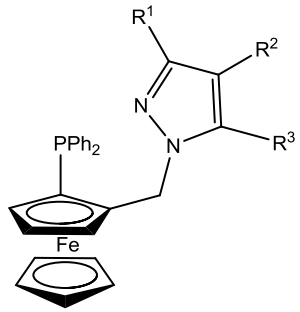
in particular, showed excellent enantioselectivities, while more bulky ligands gave poorer results, indicating that the steric properties of substituents on the 2' position have a significant influence on asymmetric induction conferred by the ligand on the reaction outcome.[31]



1.30: R = Ph
1.31: R = Me
1.32: R = *i*-Pr
1.33: R = *t*-Bu
1.34: R = Bn
1.35: R = 2-Pyridyl

1.2.3 Pyrazole-Based Ligands

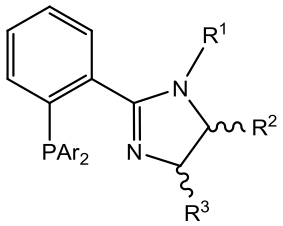
Pyrazole-containing ligands such as **1.36**, in which substituents on the phosphorus and the pyrazole ring can be easily varied allow for optimization of both steric and electronic properties of their metal complexes. This, in turn, influences their activity and selectivity in catalytic reactions. Rhodium complexes of ligand **1.36** have been used as catalysts in a number of asymmetric metal-catalyzed reactions such as hydrosilation of norbonene,[32] and hydroboration of styrene.[33] In addition to the advantages brought on by the presence of different donor groups on the metal centre, having a ferrocenyl core, which plays the important role of a spectator, on the ligand backbone gives the ligand the coordinative mobility and serves as an electron reservoir needed for pendant/donating switches.[34a] Hor and co-workers have also used this ligand backbone in their iminophosphine palladium complexes used in Suzuki-Miyaura coupling reactions.[34]



1.36

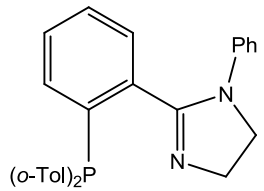
1.2.4 Imidazoline-Based Ligands

The synthesis of phosphinoimidazoline ligands such as **1.37** and their metal complexes has been reported by several groups.

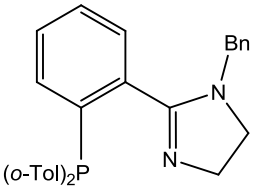


1.37

These ligands are analogous to phosphinooxazolines (see 1.2.6 below), but possess an additional nitrogen atom, which provides a further point for electronic tuning of the ligand. Pfaltz and co-workers prepared a number of these ligands and applied **1.38** and **1.39** in iridium-catalyzed hydrogenation of several alkenes.[35]

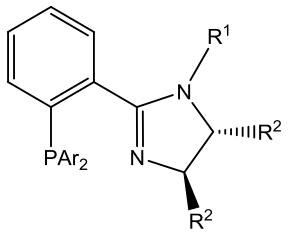


1.38



1.39

Busacca and co-workers reported the application of ligands such as **1.40** in the asymmetric intermolecular Heck reaction and made several interesting observations.[36] They observed that, 1) under the same reaction conditions, basic ligand (R^1 = Me, Bn) gave the opposite enantiomer to non-basic ligands (N-acylated); 2) ligands with alkyl substituents on the imidazoline ring gave the enantiomer opposite to that obtained with aryl-substituted ligands; and 3) there was a direct correlation between phosphine electron density and enantioselectivity.[11]

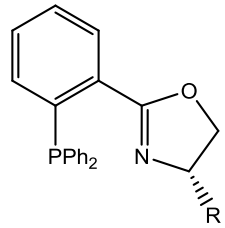


1.40: R^1 = 2-naphthyl
R^2 = Ar = 3,5-$F_2C_6H_3$

1.2.5 Oxazoline- and Thiazoline-Based Ligands

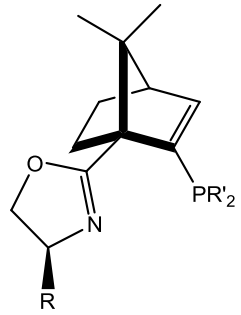
One of the most successful ligand classes is that of diphenylphosphinoaryloxazolines such as ligands **1.41** – **1.45**, which were independently reported by the groups of Pfaltz,[37] Helmchem,[38] and Williams[39] in 1993. Their palladium complexes were found to be highly efficient catalysts for allylic substitution of 1,3-diphenyl-2-propenyl acetate with a number of

different nucleophiles. The ligands have also been successful in many other asymmetric reactions with the best results coming from enantioselective Diel-Alder reactions, asymmetric intermolecular Heck reactions and the iridium-catalyzed hydrogenation of alkenes.[40]



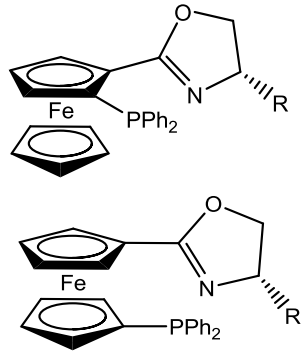
1.41: R = Me
1.42: R = *i*-Pr
1.43: R = *t*-Bu
1.44: R = Ph
1.45: R = Bn

Gilbertson and co-workers developed a series of oxazoline-containing bicyclic phosphine ligands **1.46** – **1.49**, based on ketopinic acid. These ligands have been used in palladium-catalyzed processes such as the intermolecular Heck reaction, where ligand **1.46** gave excellent enatioselectivities with a number of substrates.[41]



1.46: R = *t*-Bu; R' = Ph
1.47: R = *i*-Pr; R' = Ph
1.48: R = Ph; R' = Ph
1.49: *t*-Bu; R' = Cy

The ferrocenyl backbone structural motif has also been used by several groups in the preparation of oxazoline-based iminophosphine ligands such as ligands **1.50** – **1.55** and **1.56** - **1.58**.



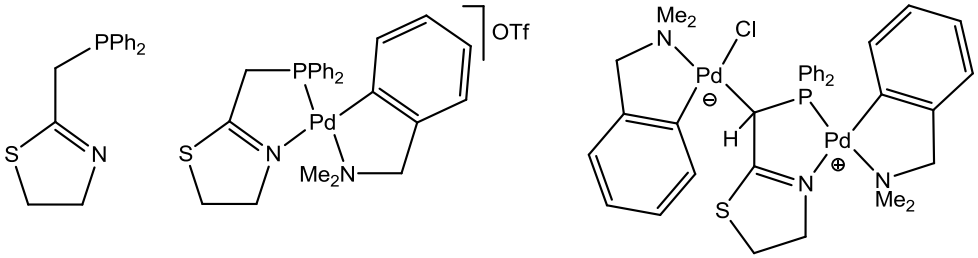
1.50: R = Me
1.51: R = *i*-Pr
1.52: R = *t*-Bu
1.53: R = Ph
1.54: R = Bn
1.55: R = *s*-Bu

1.56: R = Ph
1.57: R = *i*-Pr
1.58: R = *t*-Bu

Metal complexes formed with these ligands have been applied as catalysts in a wide range of metal-catalyzed reactions, including allylic substitutions, transfer hydrogenation of

ketones, hydrosilylation of acetophenone and intermolecular Heck reaction, among others.[42,43]

Unlike oxazoline-based iminophosphine ligands, thiazoline derivatives are not as widely reported. Brauntein and co-workers reported the synthesis and structural characterization of diphenylphosphinothiazoline **1.59** and its palladium complexes **1.60** and **1.61**.[44]



1.59 **1.60** **1.61**

1.2.6 Oxazine-Based ligands

Oxazines are six-membered ring ligands related to the oxazolines. A two-dimensional schematic of these ligands (Figure 1.2) shows that the substituent on the 4-position of both rings should be closer to the metal centre in the oxazines than it is in the oxazoline ligands.[11]

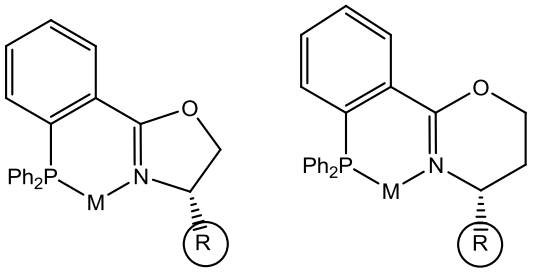
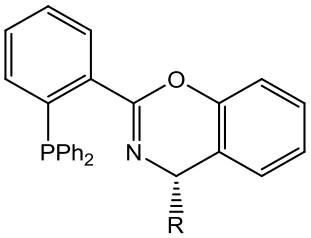


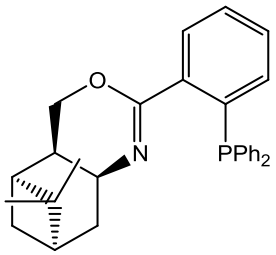
Figure 1.2: A two-dimentional schematic of oxazoline and oxazine ligands complexed to a metal centre, M.

This substituent should, therefore, exert a larger steric influence on the outcome of the reaction for metal complexes bearing oxazine ligands than for those bearing oxazoline ligands. However, while the oxazolinze ring is relatively flat, the oxazine ring can exist in both the chair- and boat- conformations, which may interfere with the efficient transfer of chirality to products. One strategy to reduce the number of possible conformations in the oxazine ring is fusing the oxazine ring to another ring. Kündig and co-workers used an aromatic ring to restrain the oxazine ring in ligands **1.62** and **1.63**. Complexes of these ligands were found to be good catalysts in a wide variety of reactions.[11,45]

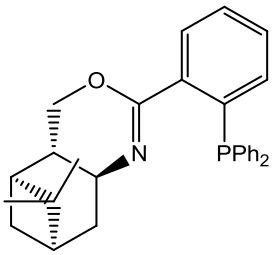


1.62: R = *t*-Bu
1.63: R = *i*-Pr

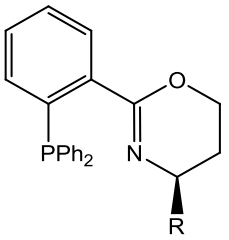
Ligands **1.64** and **1.65** reported by Evans and Brandt comprised of a β-pinene ring fused to the oxazine ring.[46]



1.64



1.65

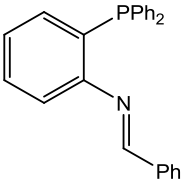


1.66

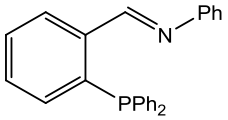
Their complexes were tested for activity in palladium-catalyzed allylic substitution of 1,3-diphenyl-2-propenyl acetate, where ligand **1.64** gave high yields and enantioselectivities over a wide range of reaction conditions.[11,47] It was also observed that under similar reactions, ligand **1.64** performed better than phosphinooxazolines.[47] The palladium complex of the unfused oxazine **1.66** gave excellent enatioselectivity in the allylic alkylation of 1,3-diphenyl-2-propenyl acetate.[47]

1.3 ACYCLIC IMINE N-DONOR LIGANDS

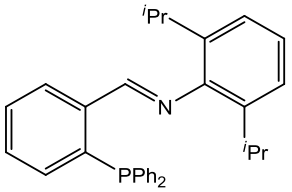
Most iminophosphine ligands in which the imine moiety is not included in a cyclic system are prepared by a condensation reaction between phosphine-bearing aldehydes/ketones such as diphenylphosphinobenzaldehyde and amines.



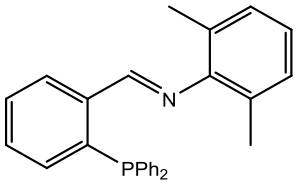
1.67



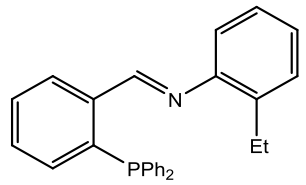
1.68



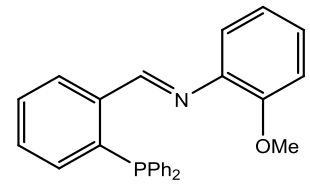
1.69



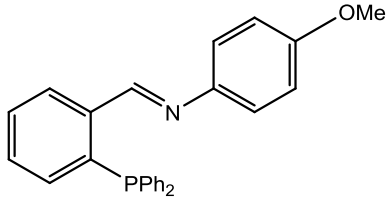
1.70



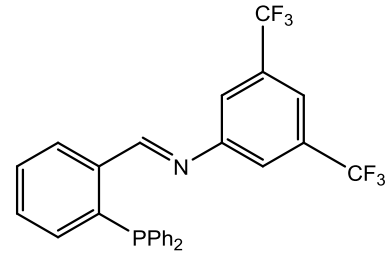
1.71



1.72



1.73



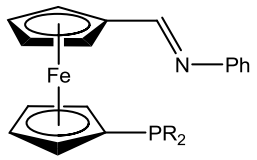
1.74

Neutral and cationic palladium methyl complexes of ligands **1.67** – **1.69** were reported by Liu and co-workers.[48] The complexes were used as catalysts for the copolymerization of ethylene and carbon monoxide. They observed that ligand **1.67**, which forms five-membered chelate rings with metal centres confers better activity toward carbonylation and copolymerization than ligands **1.68** and **1.69** which form six-membered chelate structures. Shirakawa and co-workers tested a palladium complex of ligand **1.68** for activity in the homocoupling of organostannanes using allyl acetate or air as an oxidant. Good to excellent conversions as well as isolated yields were obtained.[15b]

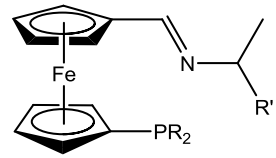
Haynes and co-workers explored the reactivity of rhodium(I) carbonyl complexes of ligands **1.67** – **1.74** with methyl iodide.[49] They observed that all complexes react with methyl iodide to give rhodium(III) methyl or acetyl complexes. Results from this study indicate that migratory CO insertion is favoured for systems in which the N-aryl group of the ligand is bulky or contains an *o*-methoxy group. For reactions involving complexes with ortho-substituted ligands **1.69**, **1.71** and **1.72**, only the acetyl complexes were obtained as products. In contrast, reactions involving ligands with no ortho-substituents on the N-aryl group, equilibrium between methyl and acetyl complexes was obtained.

Hor and co-workers prepared ligands **1.75** – **1.82** and tested their palladium complexes as catalysts in the Suzuki-Miyaura coupling reactions.[34] The ligand system was chosen because the strong (phosphine) and weak (imine) donor sites are separated by the conformationally flexible ferrocenyl moiety. This motif would enable the weak donor group to undergo facile reversible coordination to the metal centre. Both donor sites also have variable substituents, allowing the introduction of different substituents (R, and R').

Incorporation of a redox-active functionality within a ligand system potentially allows the reactivity of its metal complexes to be modulated through either chemical or electrochemical switching of the redox centre.[34c-e] In ligands **1.75** – **1.82**, the redox-active Fe(II) in the ferrocenyl backbone provides an electronic buffer that allows the catalytic metal to maintain its catalytic activity at different redox stages. Therefore it is possible to systematically and independently alter the electronic and steric properties of both donor sites. The complexes were found to be effective with good to excellent conversions being obtained even when aryl chlorides were used as substrates, with complex **1.82** giving the best results.[34b]

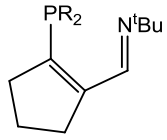


1.75: R = *t*-Bu
1.76: R = Cy
1.77: R = Ph

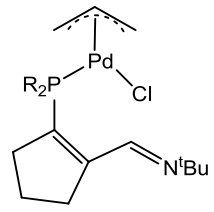


1.78: R = *t*-Bu; R' = Ph
1.79: R = *t*-Bu; R' = *p*-Tolyl
1.80: R = *t*-Bu; R = *p*-Fluorophenyl
1.81: R = *t*-Bu; R' = *m*-methoxyphenyl
1.82: R = *t*-Bu; R' = naphthyl

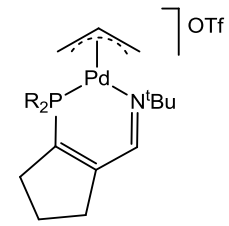
The iminophosphine ligand **1.83**, incorporating a cyclopentenyl backbone was prepared by Schmidt and co-workers, who reported the use of its palladium complexes **1.84** and **1.85**.[10,50] The cationic complexes, **1.85a** and **1.85b** showed excellent catalytic activity in the hydroamination of 3-methyl-1,2-butadiene with anilines. For complex **1.85a**, the reaction was found to be 100% atom-efficient and selective for the branched allylic amine products in high conversion at ambient temperature for non-halogenated substrates. For halogenated substrates, the hydroamination reaction was found to be efficient at 70 °C, with moderate yields. The reaction was also found to be selective for the branched product.



1.83a, 1.83b



1.84a, 1.84b

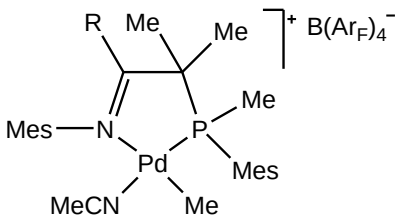


1.85a, 1.85b

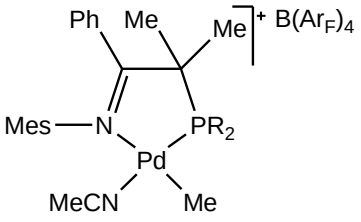
a: R = *t*-Bu
b: R = Ph

Complex **1.85a** was also found to catalyze the coupled hydroamination and aryl amino Claisen rearrangement reaction to produce substituted 2-allyl-anilines in a one-pot reaction. This two-step, one-pot reaction was found to work well for a wide range of substrates originally screened for the hydroamination reaction.

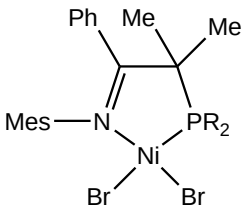
A number of palladium(II) (**1.86** – **1.89**)and nickel(II) (**1.90** – **1.94**) complexes based on bulky, non-enolizable iminophosphine ligands were reported by Daugulis and Brookhart.[51] These complexes were tested for activity as ethylene polymerization catalysts and their activity was compare to that of corresponding α-diimine complexes previously reported by the same authors. The iminophosphine complexes showed better activity and improved tempereature tolerance. The nickel complexes **1.90** – **1.93**, with *gem*-dimethyl substituent adjacent to the phosphine moiety displayed moderate activity and were found to produce substantially higher molecular weight polymers than analogous enolizable complexes.



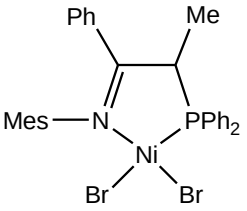
1.86: R = H
1.87: R = Ph



1.88: R = Me
1.89: R = Ph



1.90: R = Me
1.91: R = Ph
1.92: R = Me, Mes
1.93: R = *o*-Tol

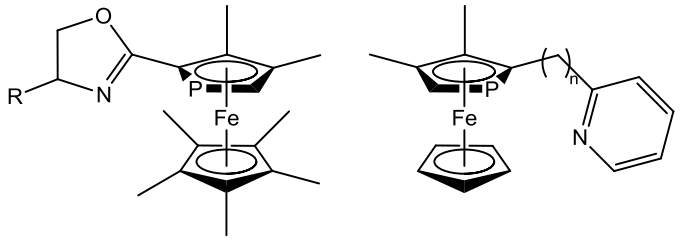


1.94

1.4 PHOSPHOLANE-BASED LIGANDS

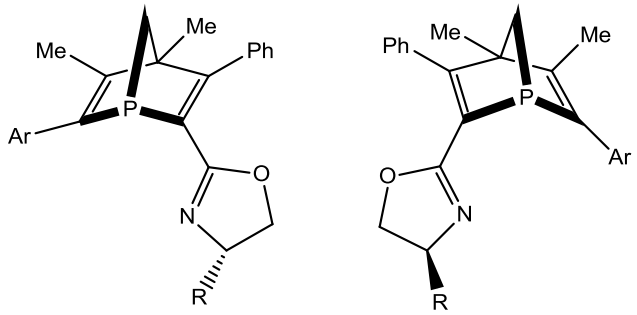
There have been a number of reports on iminophospine ligands bearing a stereogenic phosphorus atom incorporated in a cyclic structure. A class of these is the phosphaferrocenyl ligands, in which the phosphorus atom is part of the Cp ring. The ligands coordinate in a bidentate fashion, via the phosphorus and nitrogen atoms, to their metal centres. The rationale behind the design of this type of ligand is that once the metal centre coordinates, it will be in close proximity to the element of planar chiraity of the ligand, allowing the transfer of chirality in asymmetric reactions. The phosphorus atom in these systems has the electronic character of an sp^2-centre and is strongly π-accepting.[11]

Fu *et al*.[52] and Ganter *et al*.[53] reported the preparation of ligands **1.95** - **1.96**, and their application in palladium-catalyzed allylic alkylation of 1,3-diphenyl-2-propenyl acetate. While all the ligands tested showed activity, the best results were obtained when ligands **1.95** and **1.95**, bearing the oxazoline functionality were used. Excellent yields and enantioselectivities were obtained with these ligands than with **1.97** and **1.98**.



1.95: R = *i*-Pr
1.96: R = *t*-Bu
1.97: n = 1
1.98: n = 2

Ligands **1.99** – **1.102** were synthesized and used in the palladium-catalyzed allylic alkylation and Heck cross coupling reactions by Gilbertson and co-workers.[54] Ligand **1.100a** was found to be an efficient ligand in the Heck reaction between 2,3-dihydrofuran and cyclohexenyl triflate. **1.99a** and **1.100a** gave excellent conversions and high enantioselectivities in the allylic alkylation of 1,3-diphenylallyl acetate.



a **b**

1.99a, **1.99b**: Ar = Ph, R = *i*-Pr
1.100a, **1.100b**: Ar = Ph, R = *t*-Bu
1.101a, **1.101b**: Ar = Phenanthryl, R = *i*-Pr
1.102a, **1.102b**: Ar = Anthracyl, R = *i*-Pr

1.5 SUMMARY

The use of heterodonor, hemilabile ligands in synthesis and catalysis continues to be a rapidly growing area of research. Of the commonly used heterodonor ligands, those bearing phosphorus and nitrogen as their donor atoms have attracted a lot of attention due to the unique steric and electronic properties they confer to their metal complexes. In particular, iminophosphine ligands have found wide applicability in organometallic synthesis and homogenous catalysis. This brief review has highlighted the wide variety of structural motifs

found in the design of iminophosphine ligands. In addition, attention has been paid to the broad range of catalytic processes in which metal complexes bearing iminophosphine ligands have been used as catalysts.

1.6 REFERENCES

1. Braunstein, P. and Naud, F., *Angew. Chem. Int. Ed.*, 2001, **40**, 680.
2. Grützmacher, H., *Angew. Chem. Int. Ed.*, 2008, **47**, 1814.
3. Jeffrey, J. C. and Rauchfuss, T. B., *Inorg. Chem.*, 1979, **18**, 2658.
4. Espinet, P. and Soulantica, K., *Coord. Chem. Rev.*, 1999, **193 – 195**, 499.
5. Bhattacharyya, P., Parr, P. B. J. and Slawin, A. M., *J. Chem. Soc., Dalton Trans.*, 1998, 3609.
6. Lindner, R., van den Bosch, B., Lutz, M., Reek, J. N. H. and van der Vlugt, *Organometallics*, 2011, **30**, 499.
7. (a) Faller, J. W., Chao, K.-H. and Murray, H. H., *Organometallics*, 1984, **3**, 1231. (b) Ni Dhubhnhaill, O. M., Lennon, J. and Drew, M. G. B., *Dalton Trans.*, 2005, 3213. (c) Lange, D. A. and Goldfuss, B., *Beilstein J. Org. Chem*., 2007, **3**, 36.
8. (a) Davies, J. A. and Hartley, F. R., Chem. Rev., 1979, **81**, 2658. (b) Lindner, E., Haustein. M., Mayer, H. A., Gierling, K., Fawzi, R., and Steinman, M., *Organometallics*, 1995, **14**, 2246. (c) Higgins, T. B. and Mirkin, C. A., *Inorg. Chim. Acta*, 1995, **240**, 347.
9. Reddy, K. R., Tsai, W-W., Surekha, K., Lee, G-H., Peng, S-M., Chen, J-T. and Liu, S-T., *J. Chem. Soc., Dalton, Trans.*, 2002, 1776.
10. (a) Shaffer, A. R. and Schmidt, J. A. R., *Organometallics*, 2008, **27**, 1259. (b) Shaffer, A. R. and Schmidt, A. R., *Organometallics*, 2009, **28**, 2494.
11. Guiry, P. J. and Saunders, C. P., *Adv. Synth. Catal.*, 2004, **346**, 497.
12. (a)Slawin, A. M. Z., Smith M. B. and Woollins J. D., *J. Chem. Soc., Dalton Trans.*, 1996, 4575. (b) Bhattacharyya, P., Slawin, A. M. Z., Smith, M. B. and Woollins, J. D., *Inorg*. *Chem.*, 1996, **35**, 3675. (c) Slawin, A. M. Z., Smith, M. B. and Woollins, J. D., *J Chem. Soc., Dalton Trans.*, 1996, 1283. (d) Slawin, A. M. Z., Smith, M. B. and Woollins, J. D., *Polyhedron*, 1996, **15**, 1579.
13. Polosukhin, A. I., Bondarev, O. G., Korostylev, A. V., Hilgraf, R., Davankov, V. A. and Gavrilov, K. N., *Inorg. Chim. Acta.*, 2001, **323**, 55.
14. Crociani, L., Bandoli, G., Dolmella, A., Basato, M. and Corain, B., *Eur. J. Chem.*, 1998, 1811.
15. (a) Del Zotto, A., Baratta, W., Ballico M., Herdtweck, E. and Rigo, P., *Organometallics*, 2007, **26**, 5636. (b) Shirakawa, E., Nakao, Y., Murota, Y. and Hiyama, T., *J. Organomet.*

Chem., 2003, **670**, 132. (c) Crossetti, G. L., Filgueiras, C. A., Howie, R. A., Wardell, J. L. and Ziglo, C. M., *Acta Cryst.*, 2001, C**57**, 1279. (d) del Campo, O., Carbayo, A., Cuevas, J. V., Garcia-Herbaso, G. and Munoz, A., *Eur. J. Inorg. Chem*., 2009, 2254. (e) Thibault, M-H., Lucier, B. E. G., Schurko, R. W. and Fontaine, F-G., *Dalton Trans*., 2009, 7701.

16. Ghilardi, C.A., Midollini, S., Moneti, S., Orlandini, A. and Scapacci, G., *J. Chem. Soc., Dalton Trans.*, 1992, 3371.
17. Doherty, S., Knight, J. G., Scanlan, T. H., Elsegood, M. R. J. and Clegg, W., *J. Organomet. Chem.*, 2002, 650, 231.
18. MacIsaac, D. I., Geier, S. J., Vogel, C. M., Decken, A. and Westcott, S. A., *Inorg. Chim. Acta*, 2006, 359, 2771.
19. a) Christ, L. M., Zablocka, M., Spencer, S., Lavender, R., Lemaire, M. and Majoral, J. P., *J. Mol. Catal. A: Chem.*, 2006, 245, 210. b) Durry, W. J. III, Zimmermann, N., Keenan, M., Hayashi, M., Kaiser, S., Goddard, R. and Pfaltz, A., *Angew. Chem. Int. Ed.*, 2004, 43, 70. c) Crochet, P., Gimeno, J., Borge, J. and Garcia-Granda, S., *New J. Chem.*, 2003, 27, 414.
20. Casares, J. A., Espinet, P., Hernando, R., Iturbe, G., Villafane, F., Ellis, D. D. and Orpen, A. G., *Inorg. Chem*., 1997, **36**, 44.
21. (a)Bonnet, M. C., Dahan, F., Ecke, A., Keim, W., Shulz, R. P. and Tkatchenko, I., *J. Chem. Soc. Chem. Commun.*, 1994, 615. (b) Ecke, A., Keim, W., Bonnet, M. C., Tkachenko, I. and Dahan, F., *Organometallics*, 1995, **15**, 5032. (c) Drent, E., Arnoldy, P. and Budzelaar, P. H. M., *J.Organomet. Chem*., 1994, **475**, 57. (d) Drent, E., Arnoldy, P. and Budzelaar, P. H. M., *J. Organomet. Chem*., 1993, **455**, 247.
22. Deeming, A. J., Rothwell, I. P., Hursthouse, M. B. and Malik, K. M. A., *J. Chem. Soc. Dalton Trans.*, 1980, 1974.
23. Mothes, E., Sentets, S., Luquin, M. A., Mathieu, R., Lugan, N. and Lavigne, G., *Organometallics*, 2008, **27**, 1193.
24. Alcock, N. W., Brown, J. M., Pearsons, M. and Woodward, S., *Tetrahedron: Asymmetry*, 1992, **3**, 17.
25. Flapper, J., Kooijman, H., Lutz, M., Spek, A. L., van Leeuwen, P. W. N. M., Elsevier, C. J. and Kamer, P. C. J., *Organometallics*, 2009, **28**, 1180.
26. Sirbu, D., Consiglio, G. and Gischig, S., *J. Organomet. Chem.*, 2006, **691**, 1143.
27. Rülke, R. E., Kaasjager, V. E., Wehman, P., Elsevier, C. J., van Leeuwen, P. V. N. M., Vrieze, K., Fraanje, J., Goubitz, K. and Spek, A. L., *Organometallics*, 1996, **15**, 3022.
28. Crochet, P., Gimeno, J., Garcia-Granda, S. and Borge, J., *Organometallics*, 2001, **20**, 4369.
29. Chen, H.-P., Liu, Y.-H., Peng, S.-M. and Liu, S.-T., *Organometallics*, 2003, **22**, 4839.

30. Chen, J. T., Liu, S.-T. and Zhao, K.-Q., *J. Chin. Chem. Soc*., 2000, **47**, 279.
31. (a) Lacey, P. M., McDonell, C.M. and Guiry, P. J., *Tetrahedron Lett.*, 2000, **41**, 2475. (b) McCarthy, M., Goddard, R. and Guiry, P. J., *Tetrahedron: Asymmetry*, 1999, **10**, 2797.
32. Pioda, G. and Togni, A., *Tetrahedron: Asymmetry*, 1998, **9**, 3903.
33. (a) Schnyder, A., Hintermann, L. and Togni, A., *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 391. (b) Schnyder, A., Tongi, A. and Wiesli, U., *Organometallics*, 1997, **16**, 225.
34. (a) Weng, Z., Teo, S. and Hor, T. S. A., *Acc. Chem. Res*., 2007, **40**, 676. (b) Teo, S., Weng, Z. and Hor, T. S. A., *J. Organomet. Chem*., 2011, **696**, 2928. (c) Gregson, C. K. A., Gibson, V. C., Long, N. J., Marshall, E. L., Oxford, P. J. and White, A. J. P., *J. Am. Chem. Soc.*, 2006, **128**, 7410. (d) Allgeier, A. M. and Mirkin, A., *Angew. Chem., Int. Ed*., 1998, **37**, 894. (e) Lorkovic, I. M., Duff, R. R., Jr. and Wrighton, M. S., *J. Am. Chem. Soc*., 1995, **117**, 3617.
35. Menges, F., Neuburger, M. and Pfaltz, A., *Org. Lett*., 2002, **4**, 4713.
36. Busacca, C. A., Grossbach, D., So, R. C., O'Brien, E. M and Spinelli, E. M., *Org. Lett*., 2003, **5**, 595.
37. von Matt, P. and Pfaltz, A., *Angew. Chem. Int. Ed. Engl*., 1993, **32**, 566.
38. Sprinz, J. and Helmchen, G., *Tetrahedron Lett.*, 1993, **34**, 1769.
39. Dawson, G. J., Frodt, C. G., Williams, J. M. J. and Coote, S. J., *Tetrahedron Lett*., 1993, **34,** 3149.
40. (a) Helmchen, G. and Pfaltz, A., *Acc. Chem. Res*., 2000, **33**, 336. (b) Pfaltz, A. *Chimia*, 2001, **55**, 708. (c) Hiroi, K. and Watanabe, K., *Tetrahedron: Asymmetry*, 2002, **13**, 1841.
41. Gilbertson, S. R. and Fu, Z., *Org. Lett*., 2001, **3**, 161.
42. (a) Sammakia, T. and Latham, H. A., *J. Org. Chem*., 1995, **60**, 6002. (b) Richards, C. J. and Locke, A. J., *Tetrahedron: Asymmetry*, 1998, **9**, 2377. (c) Zhang, W., Hirao, T. and Ikeda, I., *Tetrahedron Lett*., 1996, **37**, 4545. (d) Malone, Y. M. and Guiry, P. J., *J. Organomet. Chem*., 2000, **603**, 110. (e) Hennessy, A. J., Malone, Y. M. and Guiry, P. J., Tetrahedron Lett., 1999, **40**, 9163. (f) Hennessy, A. J., Malone, Y. M. and Guiry, P. J., *Tetrahedron Lett*., 1999, **41**, 2261. (g) Sammakia, T. and Strangeland, E. L., *J. Org. Chem*., 1997, **62**, 6104.
43. (a) Nishibayashi, Y., Takei, I., Uemura, S. and Hidai, M., *Organometallics*, 1999, **18**, 2291. (b) Nishibayashi, Y., Segawa, K., Ohe, K. and Uemura, S., *Organometallics*, 1995, **14**, 5486. (c) Nishibayashi, Y., Segawa, K., Takada, H., Ohe, K. and Uemura, S., *Chem. Commun*., 1996, **14**, 847. (d) Nishibayashi, Y., Takei, I., Uemura, S. and Hidai, M., *Organometallics*, 1998, **17**, 3420. (e) Takei, I., Nishibayashi, Y., Ishii, Y., Mizobe, I., Uemura, S. and Hidai, M., *Chem. Commun.*, 2001, 2360. (f) Zhang, W., Yoneda, Y., Kida, T., Nakatsuji, Y. and Ikeda, I., *Tetrahedron: Asymmetry*, 1998, **9**, 3373. (g) Park,

J., Quan, Z., Lee, S., Ahn, K. H. and Cho, C. W., *J. Organomet. Chem*., 1999, **584**, 140. (h) Deng, W. P., Hou, X. L., Dai, L. X., Yu, Y. H. and Xia, W., *Chem. Commun*., 2000, 285. (i) Deng, W. P., You, S. L., Hou, X. L., Dai, L. X., Yu, Y. H., Xia, W. and Sun, J., *J. Am. Chem. Soc*., 2001, **123**, 6508. (j) You, S. L., Hou, X. L., Dai, L. X., Yu, Y. H. and Xia, W., *J. Org. Chem*., 2002, **67**, 4684. (k) Manoury, E., Fossey, J. S., Aït-Haddou, H., Daran, J. C. and Balavoine, G. G. A., *Organometallics*, 2000, **19**, 3736. (l) Deng, W. P., Hou, X. L., Dai, L. X. and Dong, X. W., *Chem. Commun*., 2000, 1483.

44. Pattacini, R., Margraf, G., Messaoudi, A., Oberbeckmann-Winter, N. and Braunstein, P., *Inorg. Chem*., 2008, **47**, 9886.
45. (a) Kündig, E. P. ans Meier, P., *Helv. Chim. Acta*, 1999, **82**, 1360. (b) Pfaltz, A., Radkowski, A., Zimmermann, N. and Zehnder, M., *Helv. Chim. Acta*, 2000, **84**, 3233.
46. Evans, P. A. and Brandt, T. A., *Tetrahedron Lett*., 1996, **37**, 9143.
47. Liu, S., Muller, J. F. K., Neuburger, M., Schaffner, S. and Zehnder, M., *Helv. Chim. Acta*, 2000, **83**, 1256.
48. Reddy, K. R., Tsai, W.-W., Surekha, K., Lee, G.-H., Peng, S.-M., Chen, J.-T. and Liu, S.-T., *J. Chem. Soc., Dalton Trans*., 2002, 1776.
49. Best, J., Wilson, J. M., Adams, H., Gonsalvi, L., Peruzzini, M. and Hayes, A., *Organometallics*, 2007, **26**, 1960.
50. Beck, J. F. and Schmidt, J. A. R., *RSC Adv*., 2012, **2**, 128.
51. Daugulis, O. and Brookhart, M., *Organometalics*, 2002, **21**, 5926.
52. Shintani, R., Lo, M. M. C. and Fu, G. C., *Org. Lett*., 2000, **2**, 3695.
53. Ganter, C., Glinsbockel, C. and Ganter, B., Eur*. J. Chem*., 1998, 1163.
54. Gilbertson, S. R., Genov, D. G. and Rheingold, A. L., *Org. Lett*., 2000, **2**, 2885.